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20. Abstract $10 + 0 + 1u)8+1$ Power (CC)

Doping superlattices (nipi structures) have been grown in InP using organometallic vapor phase epitaxy in an atmospheric pressure reactor using trimethylindium and phosphine in a hydrogen ambient. The n- and p-type dopants were diethyltellurium and dimethylzinc, respectively. The 4°K photoluminescence spectra at various excitation intensities are presented for a structure consisting of six 200 Å layers with doping levels of 1×10^{18} and 3×10^{18}/cm^{-3} for n- and p-layers. The luminescence peak is found to occur at energies considerably less than the band gap of InP and to move to higher energies with increased excitation intensity, as expected for doping superlattices where the band gap, which is indirect in real space, increases with increasing excited carrier concentration. The total photoluminescence signal decays in several steps, each exponential, with time constants ranging from 6×10^{-8} to 1×10^{-4} seconds at 4°K, typical of these spatially indirect band gap materials.

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DOPING SUPERLATTICES IN ORGANOMETALLIC VPE InP

J.S. Yuan*, M. Gal, P.C. Taylor and G.B. Stringfellow

Department of Materials Science and Engineerirng
and Department of Physics
University of Utah
Salt Lake City, Utah 84112

ABSTRACT

Doping superlattices (nipi structures) have been grown in InP using organometallic vapor phase epitaxy in an atmospheric pressure reactor using trimethylindium and phosphine in a hydrogen ambient. The n- and p-type dopants were diethyltellurium and dimethylzinc, respectively. The 4°K photoluminescence spectra at various excitation intensities are presented for a structure consisting of six 200Å layers with doping levels of 1×10^{18} and $2 \times 10^{18} cm^{-3}$ for the n- and p-layers. The luminescence peak is found to occur at energies considerably less than the band gap of InP and to move to higher energies with increased excitation intensity, as expected for doping superlattices where the band gap, which is indirect in real space, increases with increasing excited carrier concentration. The total photoluminescence signal decays in several steps, each exponential, with time constants ranging from 6×10^{-8} to 7×10^{-4} seconds at 4°K, typical of these spatially indirect band gap materials.

*Permanent Address: Changchun Institute of Physics, China.

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More than a decade ago Dohler(1,2) predicted that superlattice structures consisting of alternate n- and p-doped semiconductor layers would have interesting and potentially useful properties. Such doping superlattices, or "nipi" structures, were predicted to have a variable band gap depending on the concentration of free carriers in the conduction and valence bands and the layer thicknesses. The band gap was predicted to be indirect in the sense that the electrons and holes would be separated in real space. These properties promised the possibility of a variable band gap structure with very long minority carrier lifetimes. Such structures would be potentially useful for a number of device applications including tunable light sources, extremely sensitive optical detectors, and novel field effect transistors where the field would modulate both electron and hole conductivities(3).

A number of these predictions were verified by Ploog and co workers(4-6) in GaAs doping superlattices grown by molecular beam epitaxy (MBE). Recently, Yamauchi et al(7) have demonstrated that doping superlattices with tunable luminescence can be fabricated in InP grown by hydride vapor phase epitaxy. They produced structures with layer thicknesses ranging from 300 to 4000A. The photoluminescence (PL) peak position was observed to depend on both excitation intensity and well thickness, in qualitative agreement with theoretical predictions.

In this paper, we report the first doping superlattices grown by organometallic vapor phase epitaxy (OMVPE). The superlattices were grown in InP with layer thicknesses as small as 200A. The 4°K PL peak energy was found to be considerably less than the band gap of homogeneous InP and to depend on excitation intensity. The luminescence was found to decay in distinct stages, each stage being appproximately exponential, with a range of time constants from 6×10^{-8} to 7×10^{-4} seconds at 4°K, as expected for transitions which are indirect in real space between different quantum levels.

The OMVPE process was carried out in an atmospheric pressure system using trimethylindium(TMIn) and phosphine(PH_3) as transport agents. The use of TMIn avoids parasitic reaction problems encountered in atmospheric pressure OMVPE systems using triethylindium(TEIn). Excellent results have been reported using this system for not only InP(8), but also GaInAs(9), GaInP(9), and AlGaInP(10). The horizontal reactor contains the substrate sitting on a SiC coated graphite susceptor which is heated by infrared radiation from a strip lamp. The temperature is controlled by a thermocouple located inside of the susceptor, near the substrate. The plumbing is all stainless steel, welded where possible, with air actuated bellows valves and automatic flow controllers used throughout. The TMIn (obtained from Ventron/Alpha) is held in a constant temperature bubbler at 17°C, where the vapor pressure has been found to be approximately 1 Torr(12). The PH_3(Phoenix) is diluted to 10% in H_2. For these experiments the flow rate for H_2 through the TMIn sublimer was 250 sccm, the PH_3 flow rate was 500 sccm and the flow rate of the H_2 diluent was 2 liters/minute. These growth conditions have been found to yield a growth rate of 0.1 μm/minute. The (100) oriented InP substrates were etched for 4 minutes in a 5:1:1 mixture of H_2SO_4:H_2O_2:H_2O immediately prior to loading into the reactor. The substrate temperature was 600°C. The dopants used to fabricate the doping superlattice were diethyltelluride (DETe) as the n- type dopant and dimethylzinc (DMZn) as the p-type dopant. The dopants were obtained from Specialty Gas Products diluted in H_2 to concentrations of 5.45 ppm for the DETe and 500 ppm for the DMZn.

Growth of the doping superlattice was accomplished by growing the respective n- and p- layers for 7-50 seconds with a 30 second interruption of the growth between layers to produce abrupt doping profiles and to avoid the growth of highly compensated layers between the n- and p- layers. The layer thicknesses were estimated by assuming the growth rate to be independent of growth time. The doping levels were determined from the dopant partial pressures during growth using Hall effect data on thick layers to calibrate the dopant distribution coefficients(13). A number of doping superlattices have been grown in this way. This brief paper reports the PL data for a single superlattice with n- and p- layer thicknesses of 200A and doping levels of 1×10^{18} and $2\times10^{18} cm^{-3}$, respectively.

The PL was excited using the 514 nm line of an Ar^+ laser at powers ranging from 0.6 to 600 mW. The laser was focussed to a spot 100 μm in diameter, giving excitation intensities ranging from 6 to 6000 W/cm^2. The emission spectra were measured using an HR300, 0.3 μm spectrometer and a cooled S-1 photomultiplier. The sample was held in a cryostat at 4°K for the spectral measurements and also for the PL decay time measurements. The PL decay measurements were excited using the 500 nm line of an eximer pumped dye laser, and the time evolution of the total integreated luminescence intensity was measured. The excitation intensity, 1, was much higher than for the standard c.w. PL spectral measurements, (I=50 kW/cm^2).

The PL spectra are shown at various excitation intensities in Figure 1. In each case the spectrum consists of a single peak. The highest energy peak, measured at an excitation intensity of 600 mW, is located at 888 nm or 1.395 eV. This is somewhat below the free exciton emission in InP, which at °K is 1.418 eV. The peak shifts to lower energy and broadens as the excitation intensity decreases. At 0.6 mW, the peak is shifted to 1.326 eV, 69 meV lower than at the highest excitation intensity. The peak position is plotted versus excitation intensity in Figure 2. The slope of the line is similar to that reported by Yamauchi et al for 77°K PL measurements for layers doped to $5\times10^{17} cm^{-3}$ and for layer thicknesses of between 300 and 4000A. The data are also similar to those obtained for GaAs doping superlattices(5), i.e., approximately 25 meV per decade of pumping intensity. The peak positions reported here occur at lower energies than those reported by Yamauchi et al for similar layer thicknesses, presumably due to the higher doping levels of our superlattices.

The decay of the PL signal measured at 4°K is shown in Figure 3. The decay clearly has a rapid exponential stage with a time constant of less than 6×10^{-8} seconds followed by additional exponential stages with time constants of 4.5×10^{-6} and 7×10^{-4} seconds. Such extremely long decay times are expected for recombination of electrons and holes which are spatially separated(3). The discontinuities in the slope of the PL versus time may be due to changes in the carrier concentration as the different subbands become depopulated, as predicted theoretically(14).

In summary, the first doping superlattices obtained by OMVPE are reported. The structures are grown in InP in an atmospheric pressure apparatus using TMIn and PH_3. The n- and p- dopants are DETe and DMZn, respectively. The 4°K PL of a 200A doping superlattice consists of a single peak which shifts from 1.326 eV at a laser excitation intensity of 0.6 mW to 1.395 eV at 600 mW. The free exciton emission in InP at 4°K is 1.418 eV. The

PL decay consists of a series of three exponential steps with time constants ranging from 6×10^{-8} to 7×10^{-4} seconds.
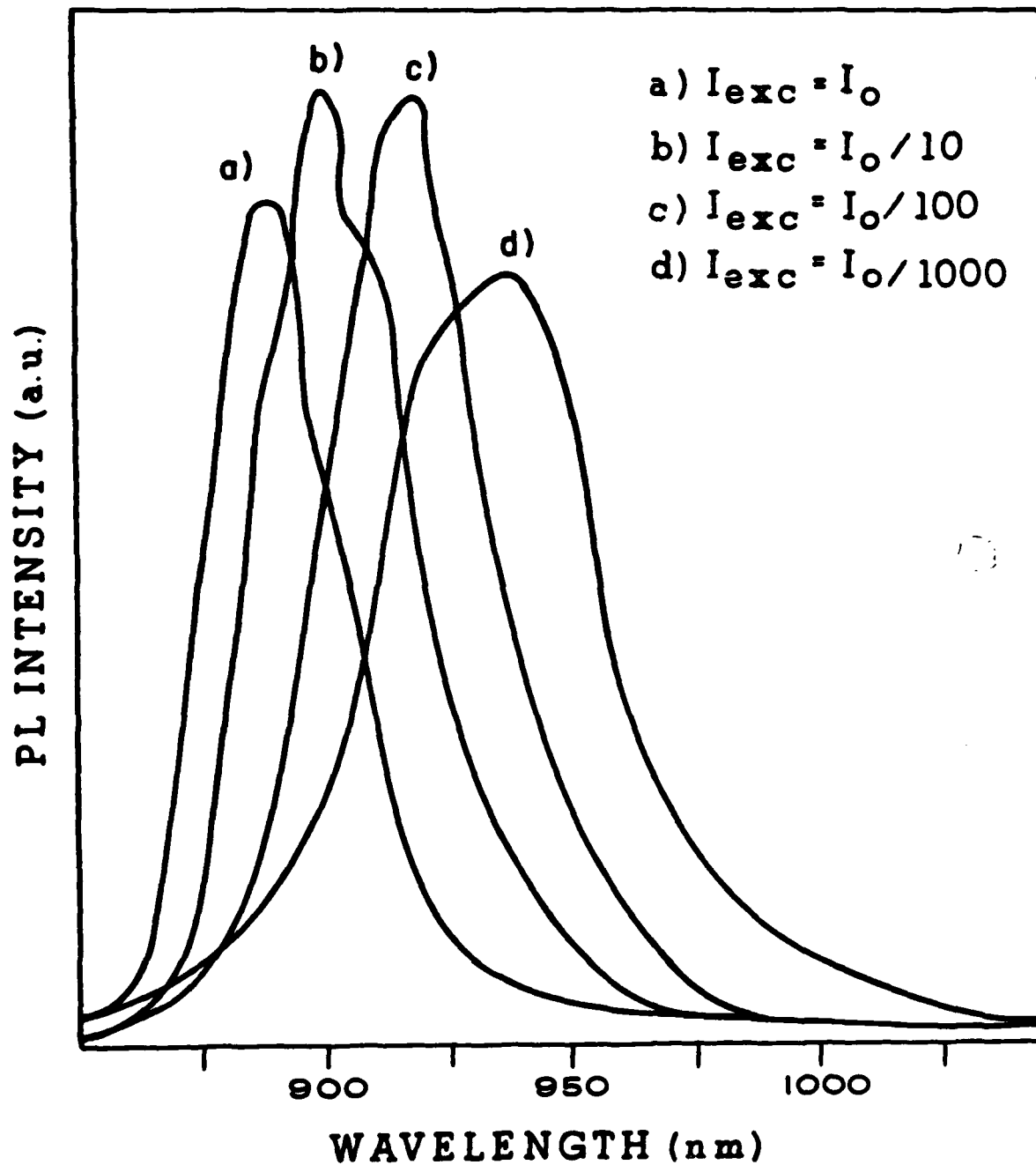
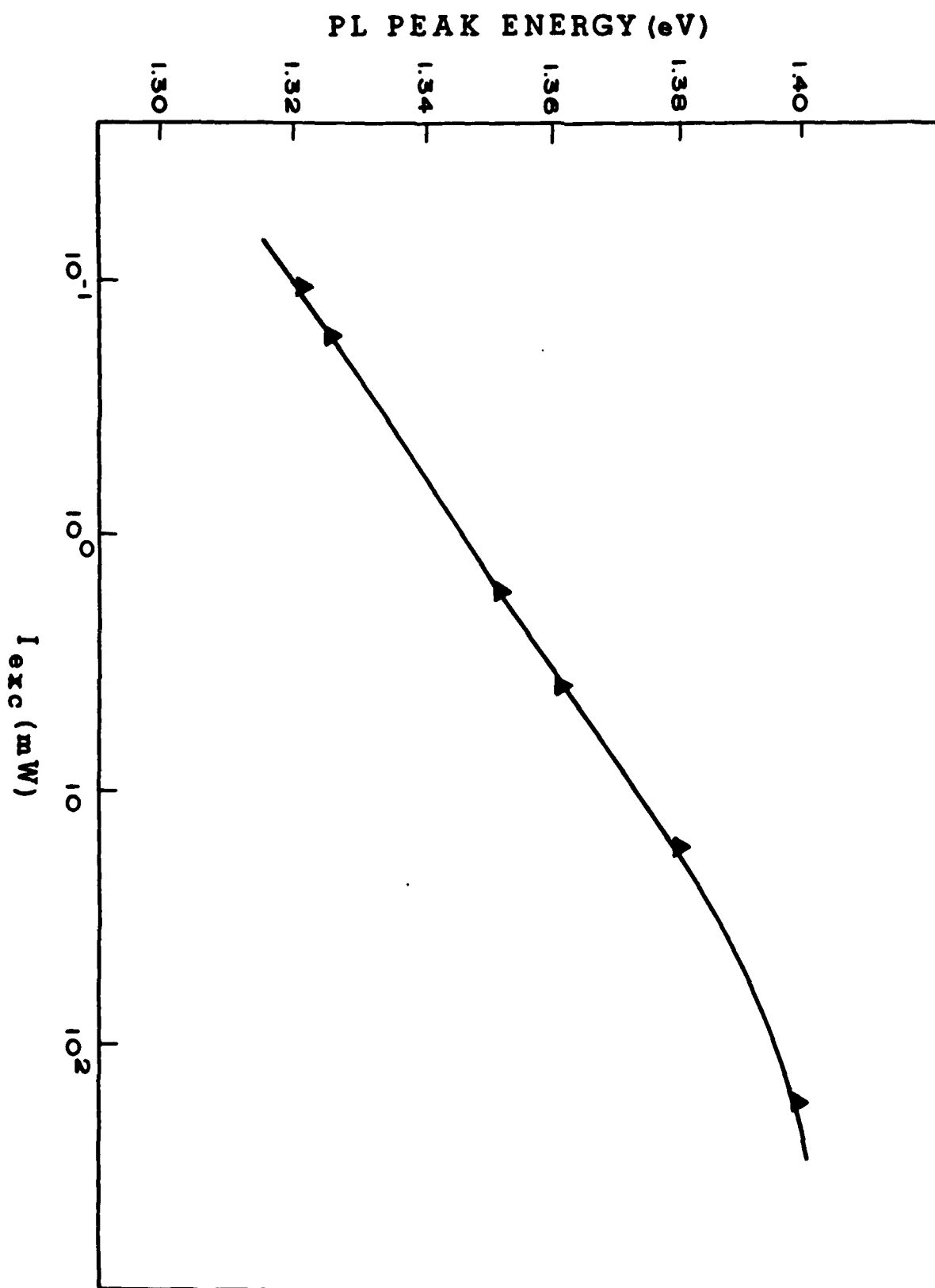## FIGURE CAPTIONS

Figure 1: Photoluminescence spectra measured at 4°K with various excitation intensities for InP doping superlattice with layer thicknesses of 200/ and n- and p-doping levels of 1×10^{18} and $2 \times 10^{18} cm^{-3}$.

Figure 2: Photoluminescence peak position versus excitation intensity.

Figure 3: Photoluminescence intensity versus time after removal of excitation.

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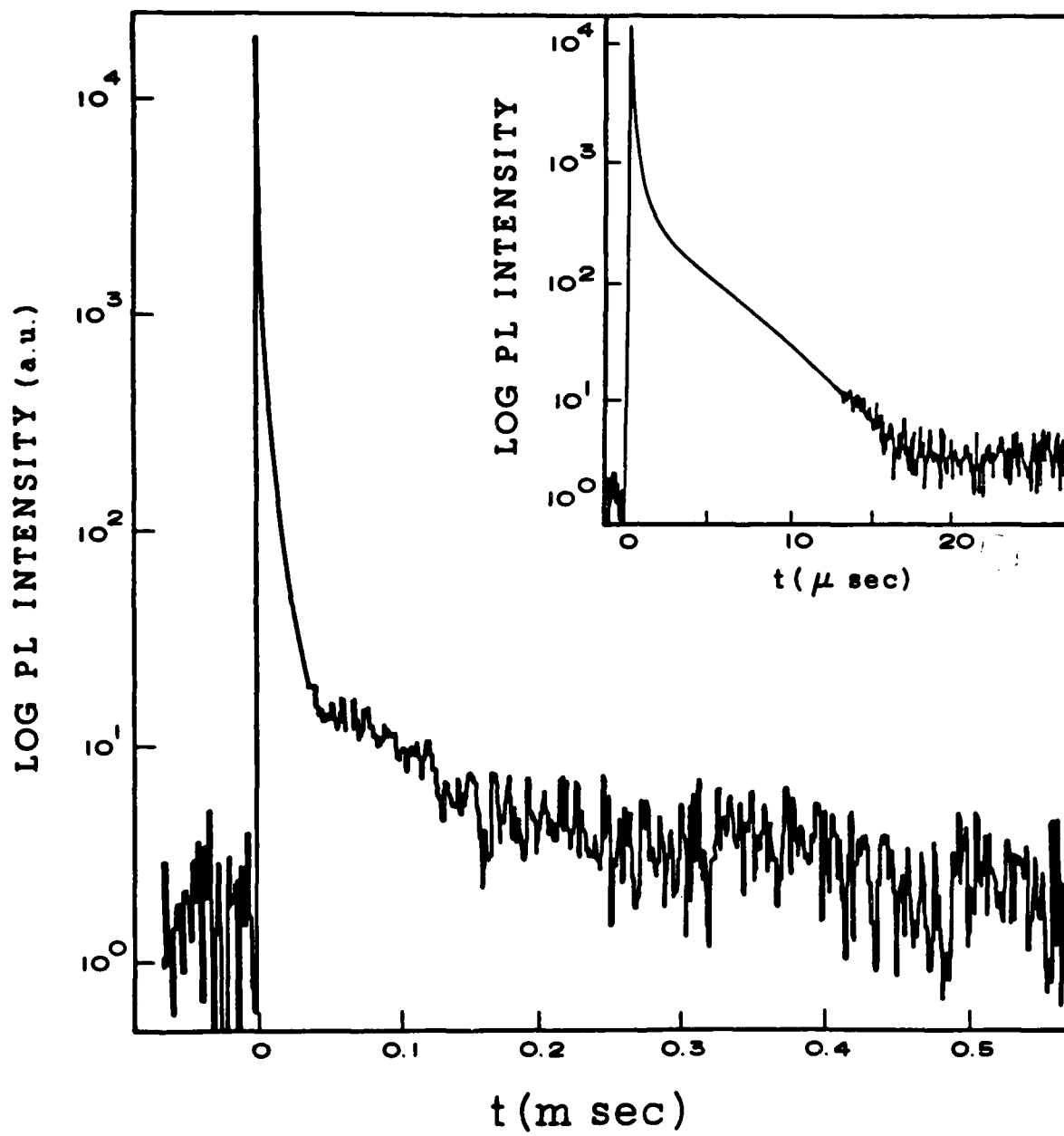14) W. Rehm, P. Ruden, G.H. Döhler and K. Ploog. Phys. Rev. B 28, 5937 (1983).

a) $I_{exc} = I_o$
b) $I_{exc} = I_o/10$
c) $I_{exc} = I_o/100$
d) $I_{exc} = I_o/1000$

PL INTENSITY (a.u.)

WAVELENGTH (nm)

Fig 3
Yuen et al

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